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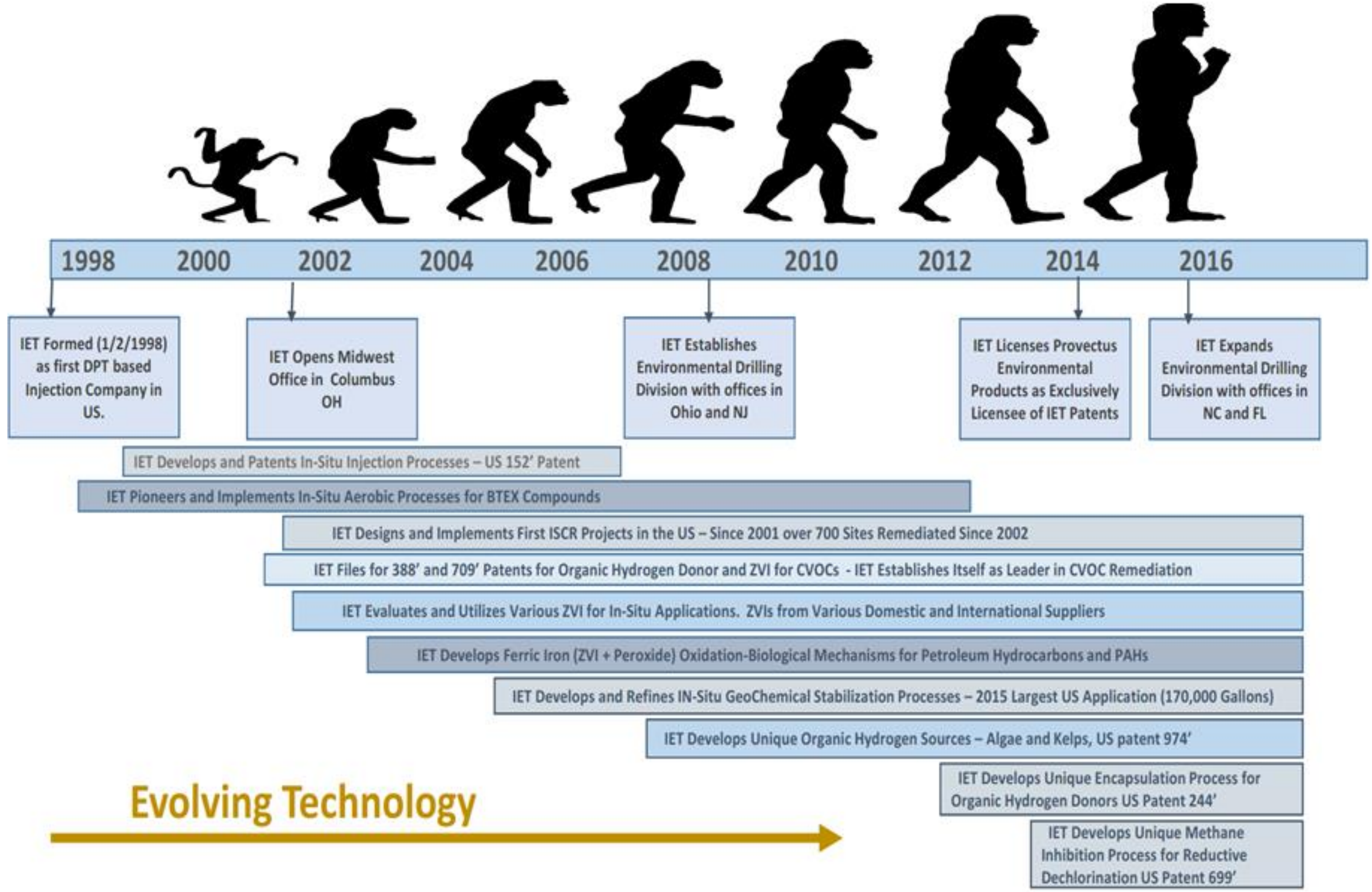
Choosing the Correct Remediation Tools From your Remediation Toolbox

Wade Meese
Vice President
Sunbury, OH

Evolution of IET



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DESIGNING

Site Evaluation – Delineation – Problem Definition – Formulation of Remedial Objectives

Compounds of Concern

Attenuation Trends

Receptors

NAPL

Preferential Pathways

Site Geochemistry

Delivery Methodology

Site Restrictions

Confining Layer(s)?

Contaminant Concentration

Contaminant Depth

Soil Type

Conceptual Model

↓

Remedial Solution Evaluation

Designing

Targeted Compounds

Petroleum Hydrocarbons

Aerobic Degradation, Chemical Oxidation, Chemical Oxidation/Anaerobic Degradation

Chlorinated Ethenes and Ethanes

Chemical Oxidation, Enhanced Reductive Dechlorination, Chemical Reduction

Heavy Metal

Precipitation via Chemical Reduction (Fe^{o}, CAPS), Solidification/Stabilization

Pesticides

Chemical Oxidation, Chemical Reduction

Creosotes/Coal Tar – PAH's

Chemical Oxidation, In-Situ Geochemical Stabilization

LNAPLS & DNAPLS

Sequestration, In-Situ Geochemical Stabilization, Abiotic Degradation

Designing

Geology – Boring Logs

BORING LOG
FO-2

PROJECT INFORMATION		DRILLING INFORMATION	
PROJECT:		DRILLING CO.:	
SITE LOCATION:		DRILLER:	
JOB NO.:		RIG TYPE:	AMS PowerProbe 9700-VTR
LOGGED BY:		DRILLING METHOD	Direct Push
DATE STARTED:	2/18/14	SAMPLING METHOD:	Macrocore - 5.0'
DATE FINISHED:	2/18/14	HAMMER WT./DROP	N/A
		COMPLETION DEPTH:	5.0'
		GROUNDWATER DEPTH:	N/A

DEPTH (feet)	SOIL LYTH	INCHES RECOV/ DRIVEN	SOIL DESCRIPTION	SAMP. NO.	SAMP. DEPTH (feet)	PID (ppm)	COMMENTS
0–5		24/60	0.0 - 5.0': Light brown medium to fine SAND			0.0	
10							
15							

NOTES: 35 degrees Fahrenheit, partly snowy

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Boring Log

Project Number:		Boring No.:	DP-2
Project Name:		Location:	
Drilling Contractor:		Logged by:	
Drilling Method: Direct Push	Date Started: 09/28/15	Total Depth (ft bgs): 26	Depth to Water (ft bgs):
Borehole Dia. (in): 2.25	Date Completed: 09/28/15	Surface Elevation (ft MSL):	

Remarks: Borehole backfilled with bentonite.

Depth (ft)	Sample No.	Sample Type	% Recovery	Graphic Log	USCS Code	Material Description	Water Level	PID Reading (ppm)	Backfill
0–0.5					OL	(0'-0.5') TOPSOIL (OL): TOPSOIL and organics.			
0.5–4			40		CL	(0.5'-4') CLAY (CL): Brown CLAY, nonplastic. Introduce some Sand.		0.0 (1), 0.0 (3)	
4–6			60		ML/SC	(4'-6') Sandy CLAY (ML/SC): Brown Sandy CLAY, fine grain, nonplastic.		0.0 (5)	
6–8	SOIL				SP	(6'-8') SAND (SP): Brown fine grain SAND with some Clay, poorly graded, moist.		0.0 (7)	
8–9					CL	(8'-9') CLAY (CL): Brown CLAY with some Sand, slightly plastic.		0.0 (9)	
9–10			65		GW	(9'-10') GRAVEL (GW): Gray fine to coarse GRAVEL.		0.0 (10)	
10–20	SOIL		80, 60		SW	(10'-20') SAND (SW): Brown fine to medium grain SAND with trace fine Gravel, well graded, moist.		0.0 (11), 0.1 (13), 0.1 (15), 0.0 (17), 0.0 (19)	
20–26	SOIL		60, 60		CL	(20'-26') CLAY (CL): Gray CLAY with trace fine Sand, nonplastic.		0.0 (21), 0.0 (23), 0.0 (25)	

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Designing

"Physical Limitations"

- Accessibility
- Water Source
- Staging of Equipment
- Staging of Remedial Materials
- Consultant/Subcontractor/Property Owner Communication
- Site Restoration
- Shipping Logistics
- Weather Conditions and Temperature

Designing

Pathways - Utilities / Historical Structures

Designing

Contributing Factors to Designing a remedial approach for a given site

“Physical Limitations”

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Designing

Understanding your site's personality

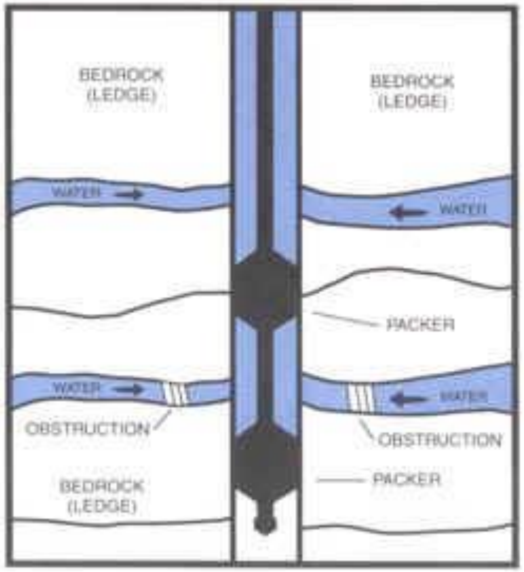





Equipment Options

Hi-Pressure Oxidants or Oils

Hi-Pressure Slurry or
Hydraulic Fracturing



Pneumatic Fracturing

Low-Pressure Application

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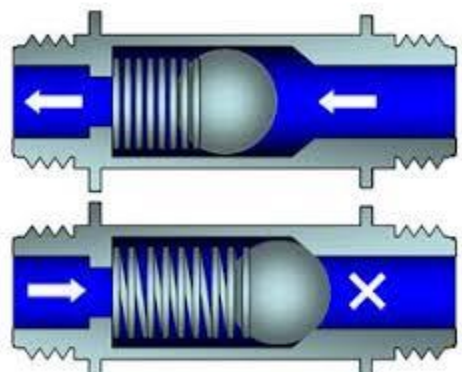
EQUIPMENT OPTIONS

IET INJECTION SYSTEM
UNITED STATES PATENT 7,044,152

Injection Trailers Include: Multiple Liquid Feed Systems, Stainless Steel Piping, Isolated Compressed Gas Containment, Safety Shower, Eyewash Station, Onboard Generator, Chemical Resistant Construction, Mobile Office Space

DPT Options

Pressure Activated Injection Probe



Delivery Process

Step #1 – Pathway Development

Compressed Gas Feed

- Confirms "Soil Break" and open delivery process
- Opens Preexisting Soil Fissures

Step #2 – Sequenced Remedial Compound Injections

Liquid #1 Feed

- Prepares Subsurface for Remedial Process
- Oxygen Scavengers under anaerobic processes
- Dilute H2O2 under Aerobic processes
- Colloidal ZVI under Fenton's Process
- pH adjusts – Calcite, Manganese Oxide, H2SO4

Step #3 – Remedial Compound(s) Injections

Liquid #2 Feed

- Viscous Liquids (lactates, butyrates)
- Hydrogen Peroxide
- Magnesium Peroxide; Calcium Peroxide
- Colloidal Suspensions – KMnO4, NaMnO4

Step #4 – Final Step

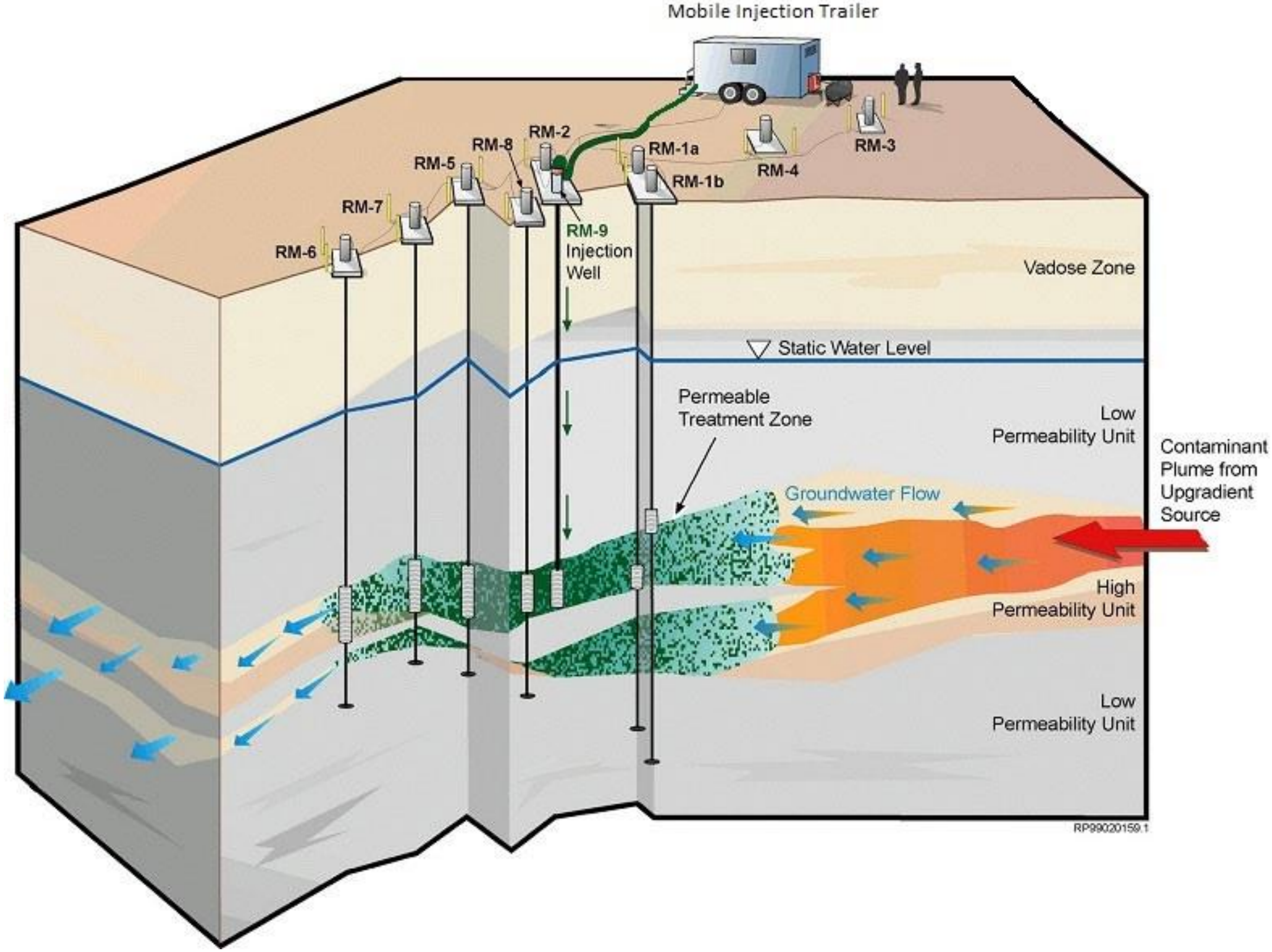
Compressed Gas Feed

- Clears Lines
- Drives materials into formation
- Prevents surface escape and spills

Completes Injection Event

PROCESS OPTIONS

Permanent Well Injection



Soil Mixing

Mobile Laboratory

The "Right" Approach

Technology Approaches

In-Situ Chemical Reduction – ISCR

- Biotic Mechanisms – Hydrogen and Electron Acceptors
- Abiotic Mechanisms – ZVI
- Methane Inhibition

Evaluation Criteria

- Methanogenesis vs Halorespiration
- Sequestration and Coelution
- Longevity vs. Release Profile
- Molar Equivalents
- Volatile Organic Fatty Acid Proportionality
- Distribution

Organic Hydrogen Donors

- Single Component Hydrogen Donors
- Vegetable Oils
- Molasses
- Lecithin
- GAC Based Amendments
- ZVI
- Mixed Hydrogen Donors

Zero-Valent Iron (ZVI)

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Diameter (microns)	Surface (m2/kg)	Particles per kilogram	Surface (m2/g)
1.0	789.5	251,297,278,566,151	0.7894737
2.0	394.7	31,412,159,820,769	0.3947368
3.0	263.2	9,307,306,613,561	0.2631579
4.0	197.4	3,926,519,977,596	0.1973684
5.0	157.9	2,010,378,228,529	0.1578947
25.0	31.6	16,083,025,828	0.0315789
50.0	15.8	2,010,378,229	0.0157895
100.0	7.9	251,297,279	0.0078947
200.0	3.9	31,412,160	0.0039474
400.0	2.0	3,926,520	0.0019737
800.0	1.0	490,815	0.0009868

Calculated for Spherical Particles of Iron

Cost Analysis

Size	Surface(M2/Kg)	Surface (Ft2/lb)	$/lb	$/100 sq. Ft
2 micron	394.7	1926.396386	9.5	$0.49
3 micron	263.2	1284.589634	7.95	$0.62
5 micron	157.9	770.6561675	6.95	$0.90
25 micron	31.6	154.2288467	3.15	$2.04
50 micron	15.8	77.11442335	2.25	$2.92
100 micron	7.9	38.55721167	1.15	$2.98
200 micron	3.9	19.03457285	0.65	$3.41
400 micron	2	9.761319411	0.45	$4.61

COMBINATION METHOD

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Oxygen Scavenger – Sodium Sulfite

Abiotic

Biotic

Anoxic Conditions

Colloidal micro ZVI

Vitamins B2 & B12

Electron Donor
- Lactate, Propionates

Butyrate, polylactateester, etc.

B12 – Catalyst for surface corrosion

Dissolved Phase Dechlorination
-Anaerobic Reactions

B12/B2 – Lowering of activation energy for electron transfer

o-PO4/NH4

Hydrogen Production

Ferrous Iron Generation
- Electron Donor
- Sulfide Precipitant
  Toxicity Reduction

o-PO4 inhibits acetotropic reactions

Essential nutrients for microbial activity

Surface Oxidation of Dissolved Phase of CVOCs

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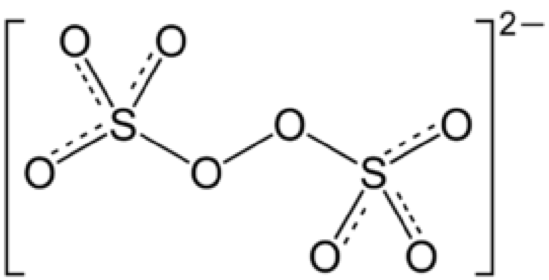
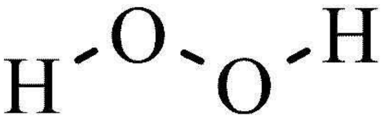
Technology Approaches

In-Situ Chemical Oxidation – ISCO

- Permanganates – Na & K
- Persulfates – Na, K, NH4
- Peroxides – H & Ca





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Oxidation Potential

Oxidant	Potential (V)	Form
Fenton's Reagent ($OH^{\bullet}$)	2.80	Liquid
Activated Persulfate ($SO_4^{-\bullet}$)	2.60	Salt/Liquid
Ferrate (Fe^{6+})	2.20	Gas
Ozone (O_3)	2.07	Gas
Persulfate ($S_2O_8^{2-}$)	2.01	Salt/Liquid
Hydrogen Peroxide (H_2O_2)	1.78	Liquid
Permanganate (MnO_4^-)	1.68	Salt ($KMnO_4$) Liquid ($NaMnO_4$)

Higher oxidation potential = stronger the oxidizer

Activation Methods

Divalent Metal Activation

- Oxidant consumption during conversion of ferrous iron to ferric iron
- Inhibition of biological utilization of the generated ferric species (EDTA)
- High oxidant consumption due to overdosing of the ferrous chelated iron

Caustic Activation

- Significant health and safety issues
- Unsuitably high (extreme) pH environment for biological attenuation
- Self-limiting biological attenuation process due to hydrogen sulfide generation

Heat Activation

- Difficult Implementation
- High Cost
- Elevated hydrogen sulfide production

Hydrogen Peroxide Activation

- Limited efficacy on many targeted compounds
- Elevated hydrogen sulfide production
- Produces heat and (excessive) gassing which can lead to surfacing issues

Rebound

The ISCO reactions are short lived

- Ozone (minutes to hours) Fenton's (hours to days) Persulfate (days to weeks) Permanganate (months).
- The ISCO process can enhance COC desorption
- Lack of secondary treatment mechanism mandates subsequent treatments

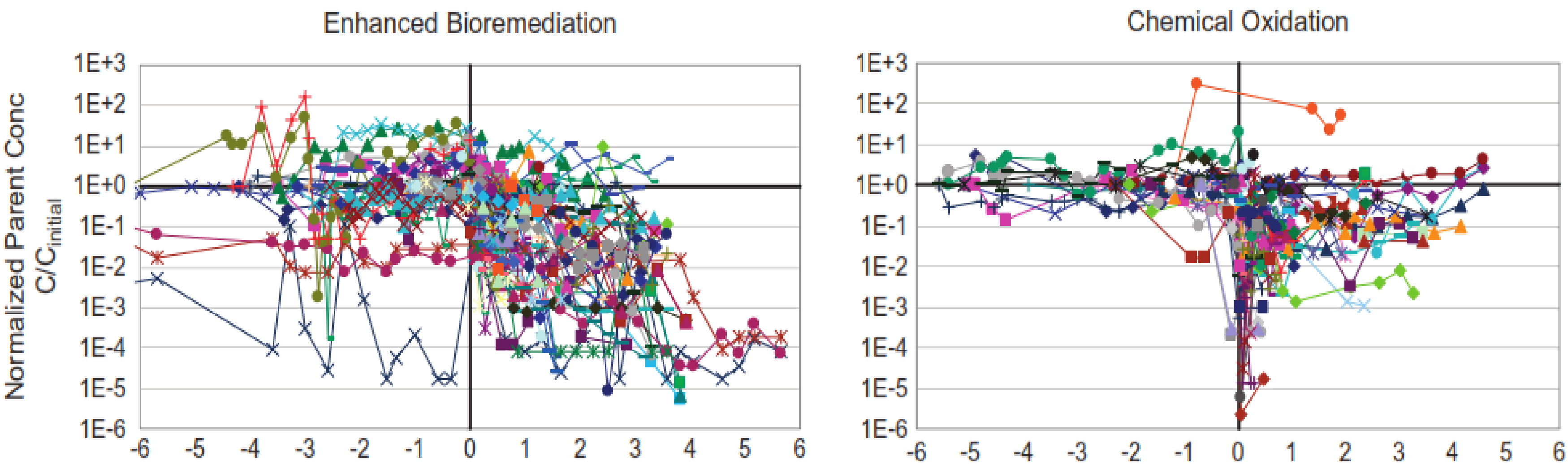


Figure 1. Temporal concentration records for wells at source depletion sites. Concentration is normalized by the initial measured concentration. Sampling time is normalized by the time of the initial source depletion treatment.

T.M. McGuire et al./ Ground Water Monitoring & Remediation 26, no. 1: 73–84 77

Oxidation with Bio Component

Sodium Persulfate + Ferric Oxide (Fe_2O_3)

- Chemical Oxidation via Sulfate ($SO_4^{\bullet}$) Radical
- Chemical Oxidation via Ferrate ($Fe^{6+\bullet}$) Radical

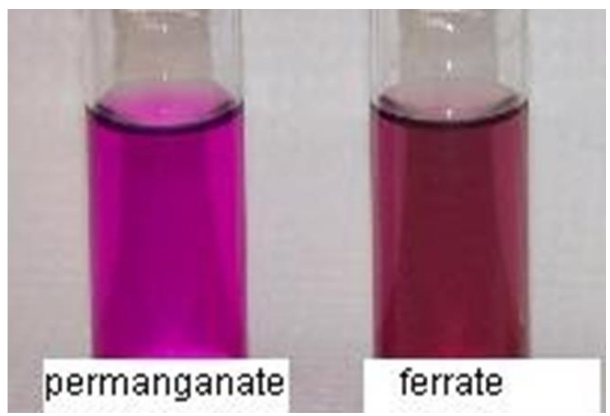
$$2\,Fe^{3+} + 3\,OCl^{-} + 4\,OH^{-} \rightarrow 2\,\mathbf{FeO_4^{2-}} + 3\,Cl^{-} + 2\,H_2O$$

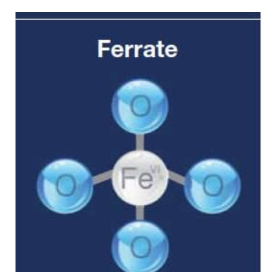
$$S_2O_8^{2-} + \text{ACTIVATOR}\,[Fe^{3+}] \rightarrow SO_4^{-}\bullet + e^{-} \rightarrow SO_4^{2-}\bullet$$

$$\mathbf{S_2O_8^{2-} + Fe^{3+} \text{---------}> Fe^{(4+\ to\ 6+)} + SO_4^{2-} + SO_4^{2-\bullet}}$$

Oxidation Potentials	Volts
Fluorine (F_2)	2.87
Hydroxyl radical ($OH\bullet$)	2.80
Persulfate radical ($SO_4\bullet$)	2.60
Ferrate (Fe^{+6})	2.20
Ozone (O_3)	2.08
Persulfate ($S_2O_8^{-2}$)	2.01
Hydrogen peroxide (H_2O_2)	1.78
Permanganate (MnO_4^{-})	1.68
Chlorine (Cl_2)	1.49

https://sites.google.com/site/ecpreparation/ferrate-vi



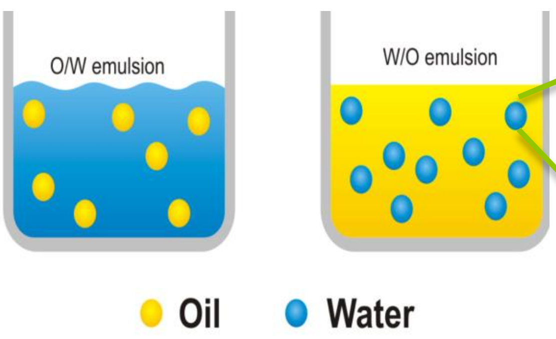


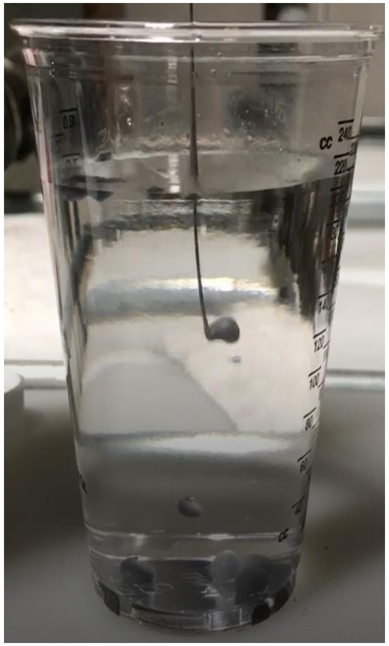
EZVI and Sequestration

What is EZVI?

- Surfactant stabilized, <u>water-in-oil</u> emulsification with small micron (< 5 μm) ZVI particles suspended in the water drops.

- EZVI is a heavier than water & hydrophobic





So You Think You Have A Solution

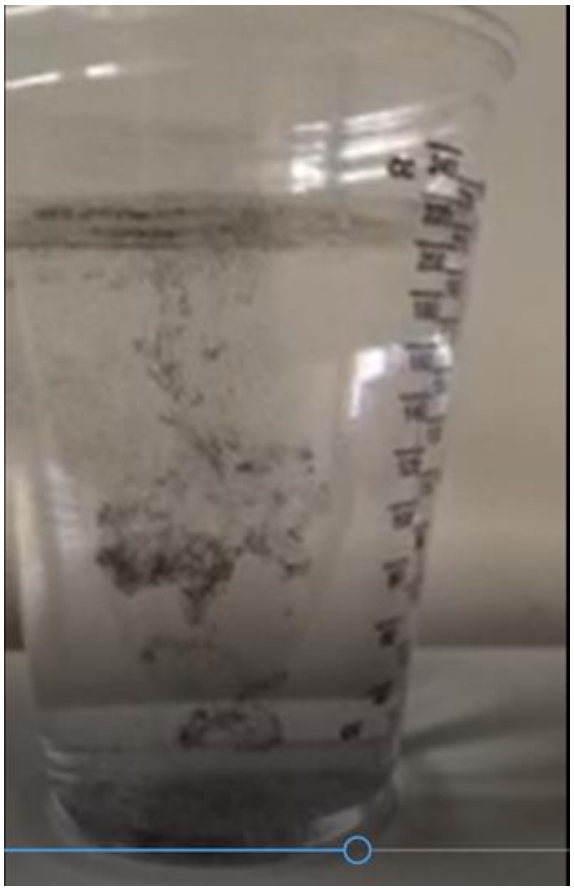
Parent Compounds

DNAPL Present

Clayey Soils

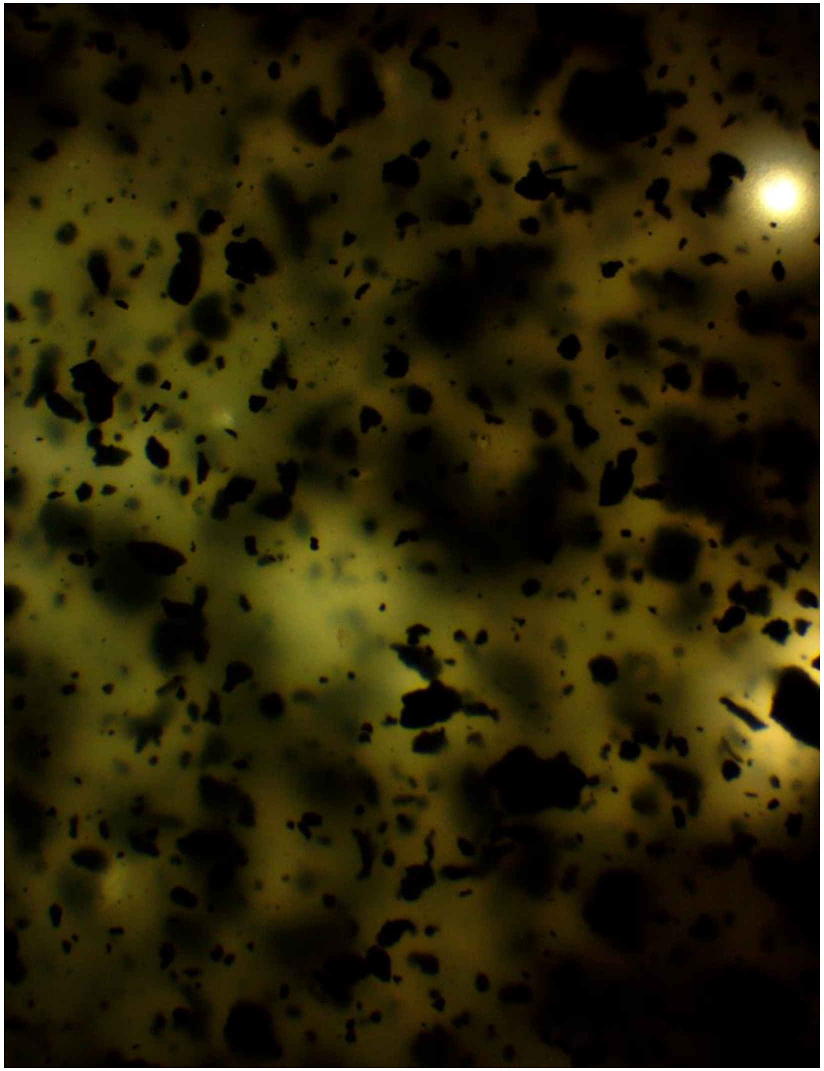
That's Not What I Wanted

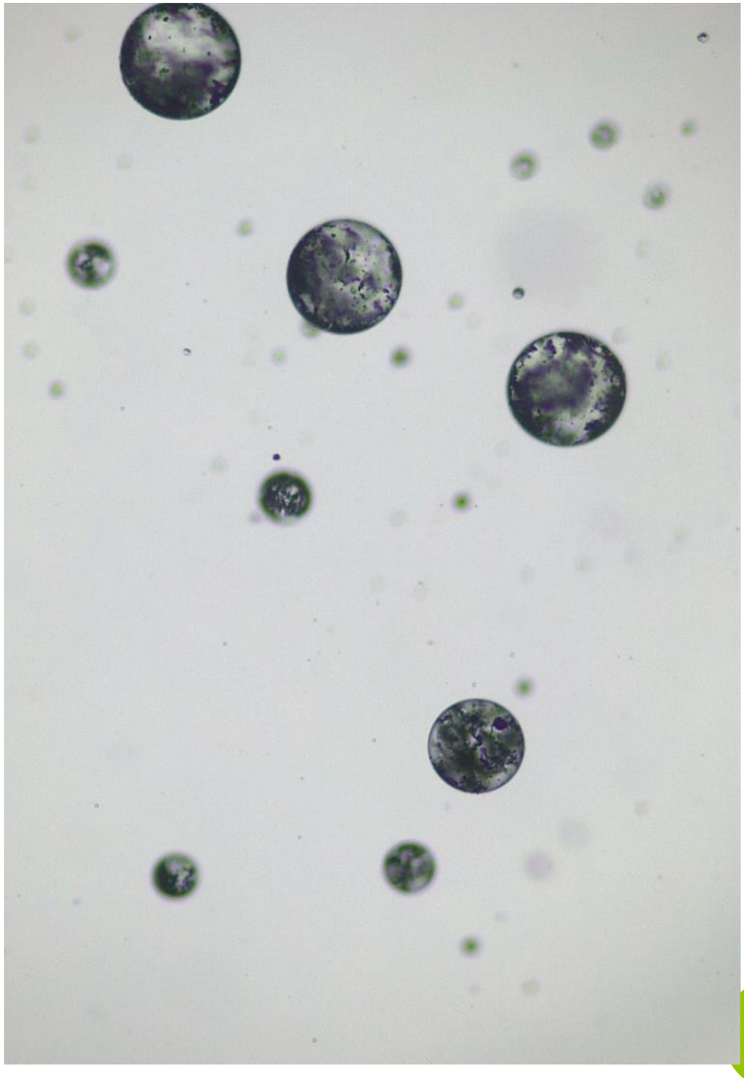
NOT-EZVI – Does NOT follow NASA patent



EZVI – Follows NASA Patent

OOPS





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QUESTIONS?